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ORIGINAL ARTICLE

Studies on kinetics and thermodynamics of oxidation of 3,4,5-trimethoxy benzaldehyde, benzaldehyde and *N,N*-dimethylamino benzaldehyde by tetraethylammonium bromochromate in dimethyl formamide and acetic acid mixture

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Abstract The oxidation of 3,4,5-trimethoxy benzaldehyde (TMBA), benzaldehyde (BA) and dimethylamino benzaldehyde (DMABA) in *N,N*-dimethyl formamide (DMF) by tetraethylammonium bromochromate (TEABC) resulted in the formation of the corresponding acids. The reaction is first order with respect to both TEABC and the aldehydes. The reaction is catalyzed by toluene-*p*-sulfonic acid (*p*-TsOH). The hydrogen ion dependence has the form: $k_{obs} = a + b$ [H$^+$]. The reaction has been studied in different percentage of DMF–acetic acid mixture. The effect of dielectric constant of the medium indicates the reaction to be of ion–dipole type. Various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of isokinetic relationship. Reason for high rate in the case of oxidation of *N,N*-dimethylamino benzaldehyde is also described. A mechanism involving formation of a chromate ester intermediate in the slow step has been proposed.

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1. Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles (Lan et al., 2005) and the determination of biological oxygen demand in

organic polluted water. Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic (Losi et al., 1994; Viamajala et al., 2004), there are continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, under mild conditions. Therefore, the search for new oxidizing agents are of interests to synthetic organic chemists. Many such reagents have been studied in recent years with some success, some of the important entries in the list of reagents are tripropylammonium fluorochromate (Mansoor and Shafi, 2010a), morpholinium chlorochromate (Malani et al., 2009), tetramethylammonium fluorochromate (Sadeghy and Ghammami, 2005), benzimidazolium fluorochromate (Mansoor and Shafi, 2014a), tributylammonium chlorochromate (Mansoor and Shafi, 2010b), tetraethylammonium chlorochromate (Mansoor and Shafi, 2015) and triethylammonium chlorochromate (Mansoor and Shafi, 2014b).

Recently tetraethylammonium bromochromate has been reported as a new and stronger oxidizing agent (Ghammamy et al., 2009). This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

The study of solute–solvent interactions in binary mixtures is more complex than in pure solvents. In a pure solvent the composition of the microsphere of solvation of a solute, the so-called cybotactic region, is the same as in the bulk solvent, but in binary mixtures the composition in this microsphere can be different. The solute can interact to a different degree with the components of the mixture, and this difference in the interactions is reflected in the composition of the microsphere of solvation. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation (Bhuvaneshwari and Elango, 2005). Specific and selective oxidation of organic compounds under non aqueous conditions is an important reaction in synthetic organic chemistry.

Kinetics of oxidation of substituted benzaldehydes by various oxidizing agents have been well studied (Mansoor, 2010; Hiran et al., 2016; Mansoor and Shafi, 2009; Krishnasamy et al., 2007; Fathimajeyanthi et al., 2002; Asghar et al., 2013; Medien, 2003). However, the kinetics of oxidation of benzaldehydes by TEABC, a Cr(VI) reagent has not yet been studied. The objective of the present work includes a systematic study of the solvent effects on the oxidation of 3,4,5-trimethoxy benzaldehyde (TMBA), benzaldehyde (BA) and dimethylamino benzaldehyde (DMABA) by TEABC in different percentage of DMF–acetic acid solvent mixture, and the analysis of the data with an aim to get better insight into the mechanism of oxidation.

2. Experimental

2.1. Materials

Tetraethylammonium bromide and chromium trioxide were obtained from Fluka (Buchs, Switzerland). 3,4,5-Trimethoxy benzaldehyde (TMBA), benzaldehyde (BA) and dimethylamino benzaldehyde (DMABA) were used as substrates.

Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

2.2. Preparation of tetraethylammonium bromochromate $(C_2H_5)_4N[CrO_3Br]$

Tetraethylammonium bromochromate (TEABC) was prepared by a reported method (Ghammamy et al., 2009) as follows: To a solution of 1 g (10 mmol) CrO_3 in 25 ml acetonitrile, placed in a 100 ml beaker, tetraethylammonium bromide (2.10 g, 10 mmol) is added portion-wise with stirring. A reddish orange solid is separated and stored in the refrigerator. The solid was washed with hexane and dried under vacuum for 1 h. Yield (95%); mp 130 °C. MS (ESI): m/z 310 $(M + H)^+$. Anal. Calcd. for $C_8H_{20}BrCrNO_3$ (%): C, 30.98; H, 6.50; N, 4.52. Found: C, 30.88; H, 6.44; N, 4.48.

$$(1)$$
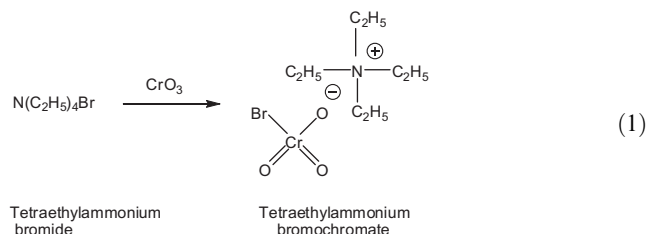
The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The chromium (VI) content may be easily determined iodometrically.

2.3. Kinetic measurements

The pseudo-first-order conditions were attained by maintaining a large excess (×15 or more) of aldehydes over TEABC. The solvent was DMF, unless specified otherwise. The reactions were followed at constant temperatures (± 0.01 K), by monitoring the decrease in [TEABC] spectrophotometrically at 366 nm using UV–VIS spectrophotometer, Shimadzu UV-1800 model. The pseudo-first-order rate constant k_{obs}, was evaluated from the linear ($r = 0.990$–0.999) plots of log [TEABC] against time for up to 80% reaction. The second order rate constant k_2, was obtained from the relation $k_2 = k_{obs}/$[Aldehyde].

2.4. Data analysis

Correlation analysis were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression) and standard deviation (SD).

2.5. Stoichiometric studies

The stoichiometric studies for the oxidation of aldehydes by TEABC were carried out with oxidant in excess. The aldehydes and TEABC were mixed in the ratio 1:3, 1:5, 1:6 and were allowed to react for 24 h at 303 K in DMF. The concentration of unreacted TEABC was determined. Δ[TEABC] was
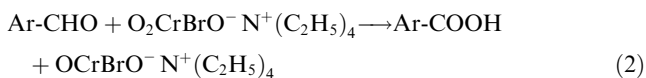
Table 1 Effect of variation of [aldehyde], [TEABC] and [H$^+$] on the rate of the reaction in DMF medium at 303 K.

10^3[TEABC] (mol dm^{-3})	10^2[Aldehyde] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^4\ k_1$ (s^{-1})		
			TMBA	BA	DMABA
0.8	3.0	0.3	9.02	15.54	36.30
1.6	3.0	0.3	9.15	15.72	36.45
2.4	3.0	0.3	9.28	15.66	36.52
3.2	3.0	0.3	9.08	15.59	36.40
4.0	3.0	0.3	9.14	15.80	36.36
1.6	0.75	0.3	2.08	3.56	9.32
1.6	1.50	0.3	4.90	7.96	18.22
1.6	2.25	0.3	7.02	11.58	27.02
1.6	3.75	0.3	11.20	19.66	45.72
1.6	4.50	0.3	13.38	23.72	54.54
1.6	3.0	0.1	5.60	9.60	21.80
1.6	3.0	0.2	7.08	11.90	29.00
1.6	3.0	0.4	12.32	19.80	49.30
1.6	3.0	0.6	16.00	26.30	63.20
1.6	3.0	0.8	21.04	34.20	82.40
1.6	3.0	0.3	9.12	15.60	36.36[a]

[a] Contained 0.001 mol dm^{-1} acrylonitrile.
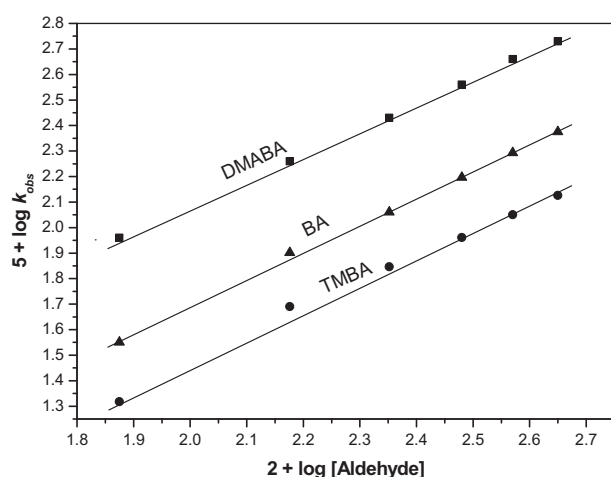
Figure 1 Showing order plot of TMBA, BA and DMABA for the oxidation of Aldehydes by TEABC.

calculated. The stoichiometry was calculated from the ratio between [Aldehyde] and [TEABC]. The reaction exhibited a 1:1 stoichiometry, i.e., one mole of the aldehydes are reacted with one mole of TEABC. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method is 3.93 ± 0.12.

Stoichiometric analysis showed that the following overall reaction.

$$\text{Ar-CHO} + \text{O}_2\text{CrBrO}^-\ \text{N}^+(\text{C}_2\text{H}_5)_4 \longrightarrow \text{Ar-COOH}$$
$$+ \text{OCrBrO}^-\ \text{N}^+(\text{C}_2\text{H}_5)_4 \qquad (2)$$

2.6. Product analysis

The oxidation of 3,4,5-trimethoxybenzaldehyde leads to the formation of 3,4,5-trimethoxy benzoic acid. The qualitative and quantitative product analyses were carried out under kinetic conditions, i.e., with an excess of the reductant. In a typical experiment, TMBA (0.3 mol) and TEABC (0.016 mol)

were made up to 50 mL with DMF and the mixture was kept in the dark for 24 h to ensure completion of the reaction in the presence of 0.3 mol dm^{-3} TsOH. After the completion of the reaction under kinetic conditions, the reaction mixture was treated with solid NaHCO$_3$ and then filtered. After complete neutralization, the reaction mixture was extracted with ether to remove unreacted TMBA. Non-aqueous layer was treated with conc. HCl drop by drop till bicarbonate was neutralized. Again ether was added with shaking. The product in ether was washed with cold water, dried and identified as 3,4,5-trimethoxybenzoic acid by melting point analysis (169 °C and this agreed with the literature value 168–171 °C), TLC (4:1 benzene–absolute alcohol) which revealed only one spot. Similar experiments were performed with benzaldehyde and N,N-dimethylamino benzaldehyde also.

3. Results and discussion

3.1. Order of reaction

The kinetics of oxidation of TMBA, BA and DMABA by TEABC was studied in DMF at 303 K in the presence of toluene-p-sulfonic acid. The reactions were of first order with respect to TEABC. Furthermore, the values of k_{obs} were independent of the initial concentration of TEABC (Table 1). Reaction rates increase linearly with increase in the concentrations of the aldehydes (Table 1). The plot of log k_1 versus log [Aldehyde] gave the slope of 1.026 ($r = 0.999$), 1.054 ($r = 0.999$) and 0.998 ($r = 0.999$), respectively, for TMBA, BA and DMABA, respectively, (Fig. 1) indicating first order with respect to substrate. Under pseudo-first-order conditions, the plot of $1/k_1$ versus $1/$[Aldehyde] were linear with a negligible intercept indicating that the intermediate formed in a slow step got consumed in a subsequent fast step.

3.2. Effect of acidity

The reaction is catalyzed by hydrogen ions (Table 1). The hydrogen ion dependence has the following form $k_{obs} = a + b$

[H$^+$]. The values of a and b, for aldehydes are determined. The values at 303 K is obtained for TMBA ($a = 2.92 \pm 0.38 \times 10^{-4}\,s^{-1}$; $b = 22.36 \pm 0.81 \times 10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$), BA ($a = 5.34 \pm 0.45 \times 10^{-4}\,s^{-1}$; $b = 35.62 \pm 0.95 \times 10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$) and DMABA ($a = 12.18 \pm 0.66 \times 10^{-4}\,s^{-1}$; $b = 87.11 \pm 1.32 \times 10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$). TEABC may become protonated in the presence of acid. The protonated TEABC may function as an effective oxidant.

$$O_2CrBrO^- N^+(C_2H_5)_4 + H^+ \rightleftharpoons (OH)OCrBrO^- N^+(C_2H_5)_4 \quad (3)$$
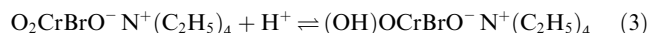
The formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar PCC (Sharma et al., 1997) and PFC (Sharma et al., 1996).

Table 2 Effect of [MnSO$_4$] on the oxidation of aldehydes by TEABC in DMF at 303 K.

10^3[MnSO$_4$] (mol dm^{-3})	$10^4\,k_1$ (s^{-1})		
	TMBA	BA	DMABA
0.0	9.15	15.72	36.45
1.0	8.66	15.12	35.34
2.0	8.34	14.66	34.66
3.0	7.96	14.08	33.78
4.0	7.42	13.66	32.56
5.0	7.06	13.02	31.72

10^2[Aldehyde] = 3.0 mol dm^{-3}; 10^3[TEABC] = 1.6 mol dm^{-3}; 10 [H$^+$] = 3.0 mol dm^{-3}.

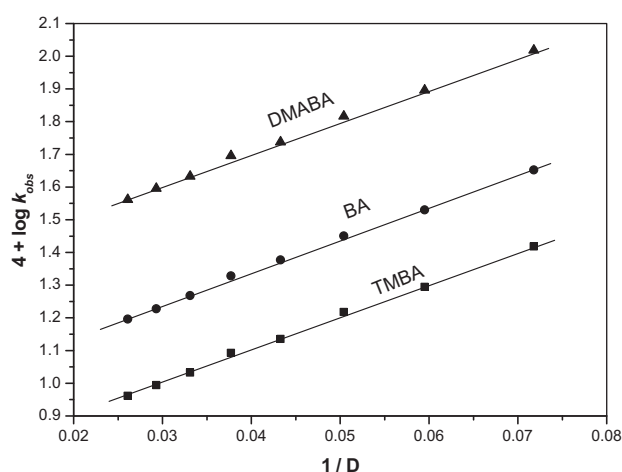**Table 3** Effect of ionic strength on the oxidation of aldehydes by TEABC in DMF at 303 K.

10^3[NaClO$_4$] (mol dm^{-3})	$10^4\,k_1$ (s^{-1})		
	TMBA	BA	DMABA
0.0	9.15	15.72	36.45
1.0	9.09	15.66	36.46
2.0	9.11	15.60	36.33
3.0	9.23	15.70	36.30
4.0	9.18	15.78	36.42
5.0	9.10	15.82	36.51
8.0	9.25	15.76	36.40
10.0	9.18	15.72	36.54

10^2[Aldehyde] = 3.0 mol dm^{-3}; 10^3[TEABC] = 1.6 mol dm^{-3}; 10 [H$^+$] = 3.0 mol dm^{-3}.

Figure 2 Plot of 1/D against logk_{obs} showing the effect of solvent polarity for the oxidation of aldehydes by TEABC.

3.3. Test for free radicals

The oxidation of TMBA, BA and DMABA, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile had no effect on the rate of oxidation (Table 1). Thus, a one – electron oxidation giving rise to free radicals is unlikely.

3.4. Effect of added MnSO$_4$ concentration

Addition of Mn(II), in the form of MnSO$_4$ by varying in the range from 0.001 to 0.005 M retards the rate of the oxidation process indicating two electron oxidation (Table 2). This indicates the involvement of Cr(IV) intermediate in the oxidation of aldehydes by Cr(VI) reagent. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV) reduces Cr(VI) to Cr(V) and the oxidation of aldehydes by Cr(V) is fast. This may be taken as evidence for the formation of Cr(IV) species and hence TEABC acts as a two-electron transfer oxidant (Karunakaran and Suesh, 2004; Bhuvaneshwari and Elango, 2006).

3.5. Effect of ionic strength

The effect of ionic strength was studied to observe the effect of salt on the rate of oxidation in Debye–Huckel limit by varying

Table 4 Effect of varying solvent polarity on the rate of the oxidation of aldehydes by TEABC at 303 K.

% Acetic acid–DMF (v/v)	Dielectric constant	1/D	$10^4\,k_1$ (s^{-1})		
			TMBA	BA	DMABA
0:100	38.30	0.0261	9.15	15.72	36.45
10:90	34.11	0.0293	9.87	16.89	39.45
20:80	30.19	0.0331	10.80	18.54	42.90
30:70	26.52	0.0377	12.42	21.30	49.62
40:60	23.08	0.0433	13.68	23.34	54.62
50:50	19.85	0.0504	16.50	28.20	65.52
60:40	16.80	0.0595	19.71	33.90	78.66
70:30	13.92	0.0718	26.22	44.88	104.21

10^2[Aldehyde] = 3.0 mol dm^{-3}; 10^3[TEABC] = 1.6 mol dm^{-3}; 10 [H$^+$] = 3.0 mol dm^{-3}.

Table 5 Second order rate constants and activation parameters and for the oxidation of aldehydes by TEABC.

% AcOH–DMF (v/v)	$10^2 k_2$ (dm^3 mol^{-1} s^{-1})				E_a	$\Delta S^{\#}$	$-\Delta H^{\#}$	$\Delta G^{\#}$
	298 K	303 K	308 K	313 K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})	(kJ mol^{-1}) (at 303 K)
TMBA								
0:100	2.15	3.05	4.27	6.11	53.78	107.04 ± 3.6	50.60 ± 1.2	83.03 ± 2.3
10:90	2.33	3.29	4.97	7.45	60.50	82.30 ± 3.9	57.82 ± 1.3	82.76 ± 2.5
20:80	2.40	3.60	5.11	7.63	59.16	85.75 ± 3.0	56.66 ± 1.0	82.64 ± 1.9
30:70	2.84	4.14	5.84	8.35	55.49	96.85 ± 2.1	52.96 ± 0.7	82.05 ± 1.3
40:60	2.99	4.56	6.84	10.19	63.38	70.24 ± 0.9	60.69 ± 0.3	81.97 ± 0.5
50:50	3.70	5.50	7.64	10.70	54.55	97.79 ± 3.3	52.07 ± 1.1	81.70 ± 2.0
60:40	4.24	6.57	9.96	14.77	64.52	63.16 ± 0.9	61.99 ± 0.3	81.13 ± 0.5
70:30	6.11	8.74	13.27	19.93	61.46	70.72 ± 4.2	58.89 ± 1.4	80.32 ± 2.6
BA								
0:100	3.50	5.24	7.27	10.34	55.49	95.03 ± 3.0	53.03 ± 1.0	81.82 ± 1.9
10:90	3.97	5.63	8.60	13.10	62.03	72.29 ± 3.9	59.54 ± 1.3	81.44 ± 2.5
20:80	4.12	6.18	8.90	13.38	60.43	77.21 ± 3.3	57.82 ± 1.1	81.21 ± 2.0
30:70	4.86	7.10	10.67	16.03	61.81	71.32 ± 3.6	59.16 ± 1.2	80.77 ± 2.2
40:60	5.11	7.78	10.97	16.40	59.56	78.28 ± 3.0	57.05 ± 1.0	80.76 ± 1.9
50:50	6.35	9.40	13.72	20.04	59.35	77.52 ± 1.8	56.76 ± 0.6	80.24 ± 1.1
60:40	7.29	11.30	17.06	25.42	64.50	52.86 ± 2.7	63.75 ± 0.9	79.76 ± 1.7
70:30	10.46	14.96	21.07	29.95	54.24	90.15 ± 2.1	51.69 ± 0.7	79.41 ± 1.3
DMABA								
0:100	8.04	12.15	18.04	27.15	62.72	63.93 ± 2.4	60.31 ± 0.8	79.68 ± 1.5
10:90	9.01	13.15	18.41	29.12	59.22	73.11 ± 3.3	57.24 ± 1.1	79.39 ± 2.0
20:80	9.63	14.30	21.30	31.54	61.27	66.99 ± 2.1	58.78 ± 0.7	79.08 ± 1.3
30:70	11.33	16.54	23.15	35.35	58.21	76.75 ± 4.8	55.52 ± 1.6	78.77 ± 3.0
40:60	12.48	18.20	27.30	40.87	61.46	64.69 ± 3.9	59.13 ± 1.3	78.73 ± 2.4
50:50	14.34	21.84	31.02	44.04	57.63	75.98 ± 3.6	55.13 ± 1.2	78.15 ± 2.2
60:40	18.34	26.22	39.35	58.15	59.93	66.60 ± 4.2	57.24 ± 1.4	77.42 ± 2.6
70:30	24.29	34.74	48.18	69.46	53.99	84.41 ± 3.3	51.31 ± 1.1	76.87 ± 2.0

10^2[Aldehyde] = 3.0 mol dm^{-3}; 10^3[TEABC] = 1.6 mol dm^{-3}; 10 [H$^+$] = 3.0 mol dm^{-3}.

concentration of NaClO$_4$ from 0.001 to 0.01 M provided other conditions being constant (Table 3). The rate of reaction remains almost unchanged while increasing the NaClO$_4$ concentration. It proves that interaction in rate determining step is not of ion–ion type (Laidler, 2005).

3.6. Effect of solvent polarity on reaction rate

The oxidation of aldehydes have been studied in the binary mixture of DMF–acetic acid mixture. For the oxidation of TMBA, BA and DMABA the reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table 4.

The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 0% to 70%. The pseudo-first-order rate constants were estimated for the oxidation of TMBA, BA and DMABA with TEABC. The reaction rate is increases markedly with the increase in the proportion of acetic acid in the medium (Table 4). When the acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The enhancement of the reaction rate with an increase in the amount of acetic acid generally may be attributed to two factors, viz, (i) the increase in acidity occurring at constant [H$^+$], and (ii) the decrease in the dielectric constant with an increase in the acetic acid content.

The plot of logk_1 versus 1/D (dielectric constant) is linear with positive slope suggesting the presence of either dipole–dipole or ion–dipole type of interaction between the oxidant and the substrate (Scatchard, 1939) (Fig. 2). Plot of logk_1 versus (D − 1)/(2D + 1) is a curvature indicating the absence of dipole–dipole interaction in the rate determining step. Positive slope of logk_1 versus 1/D plot indicates that the reaction involves a cation–dipole type of interaction in the rate determining step.

Amis (1967) holds the view that in an ion–dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate increases with the decreasing dielectric constant of the medium (Amis, 1967). Due to the polar nature of the solvent, transition state is stabilized, i.e., the polar solvent molecules surround the transition state and result in less disproportion.

3.7. Activation parameters

The kinetics of oxidation of TMBA, BA and DMABA were studied at four different temperatures, viz., 298, 303, 308 and 313 K. The second order rate constants were calculated (Table 5). The Arrhenius plot of logk_2 versus 1/T is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298,
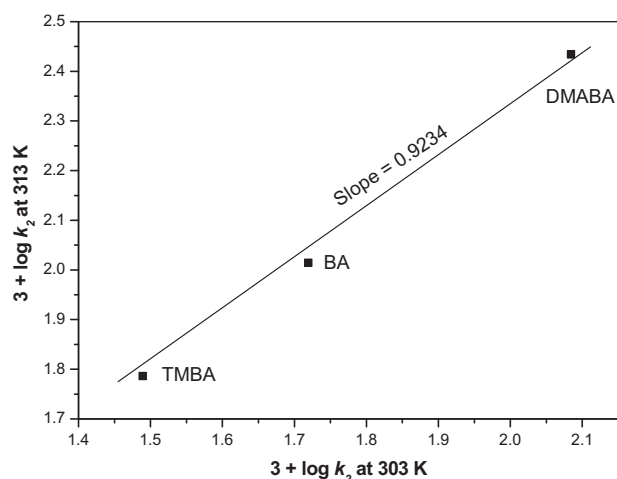
Figure 3 Exner's plot for the oxidation of aldehydes by TEABC between $3 + \log k_2$ (at 313 K) and $3 + \log k_2$ (at 303 K).

303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 5. The least square method gives the values and standard errors of enthalpy and entropy of activation respectively. Statistical analysis of the Eyring equation clearly confirms that the standard errors of $\Delta H^{\#}$ and $\Delta S^{\#}$ correlate (Lente et al., 2005). The entropy of activation is negative for aldehydes.

3.8. Isokinetic relationship

The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship.

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\#} \qquad (4)$$

The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. Exner suggested a method of testing the validity of isokinetic relationship (Bhuvaseshwari and Elango, 2007). The isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to Eq. (5).

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \qquad (5)$$

The linear relationship in Exner plots (Exner, 1964; Exner et al., 1973) at $3 + \log k_2$ (303 K) and $3 + \log k_2$ (313 K) observed in the present study imply the validity of the isokinetic relationship. Isokinetic temperature obtained is 519 K (Fig. 3). The linear isokinetic correlation implies that TMBA, BA and DMABA are oxidized by the same mechanism and the changes in the rate are governed by the changes in both the enthalpy and entropy of activation (Leffler and Grunwald, 1963). The isokinetic relationship of TMBA in different percentage of DMF–acetic acid solvent mixture is shown in Fig. 4. The existence of a linear relationship (slope = 0.9306, r = 0.997, isokinetic temperature = 561 K) between $3 + \log k_2$ (303 K) and $3 + \log k_2$ (313 K) indicates that a common mechanism is operating in all studied solvent mixture systems.
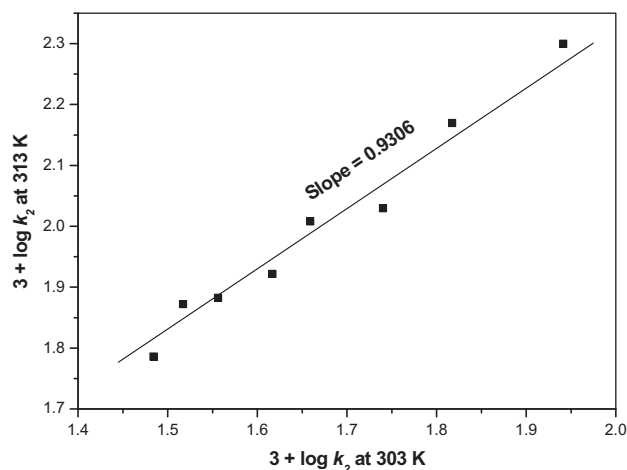

Figure 4 Exner's plot for the oxidation of TMBA by TEABC between $3 + \log k_2$ (at 313 K) and $3 + \log k_2$ (at 303 K) at various percentage of DMF–acetic acid mixture.

### 3.9. Reason for high rate in the case of oxidation of N, N-dimethylamino benzaldehyde

In the case of *N,N*-dimethylamino benzaldehyde, –N(CH$_3$)$_2$ being a electron donating group, expectation of retardation effect on the reaction rate is quite normal. But the observed reaction rate is very high in the case of oxidation of *N,N*-dimethylamino benzaldehyde. This observation can be best explained as follows: In the strong acid medium the following protonation is possible.
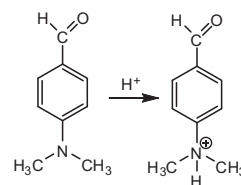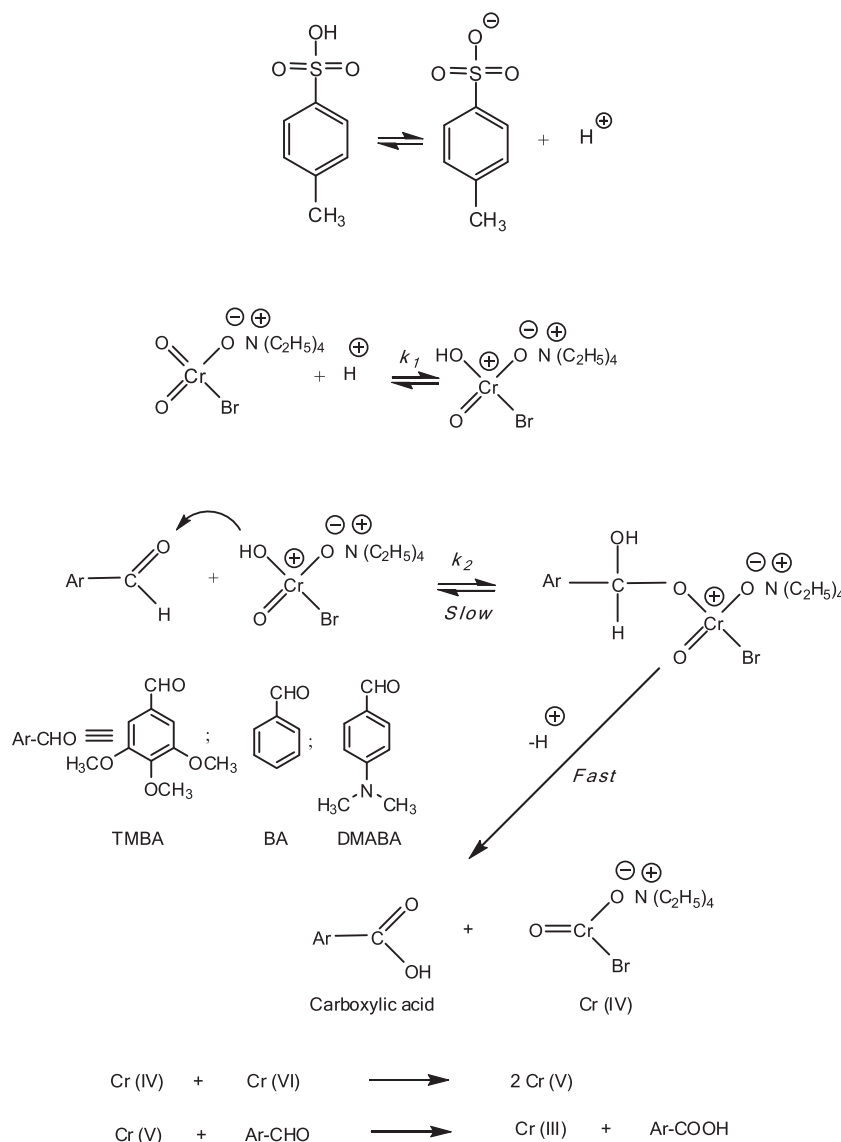

Here the $N^+H(CH_3)_2$ group act as a very strong electron-withdrawing group. Hence, it reacts at a very fast rate with the oxidant. Another possible explanation is *N,N*-dimethylamino benzaldehyde exhibiting the following resonance structures.
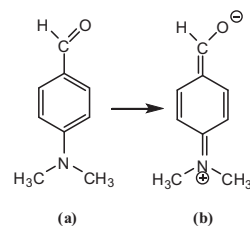
The dipolar ion (b) can be stabilized in the acid medium as follows as in (c).
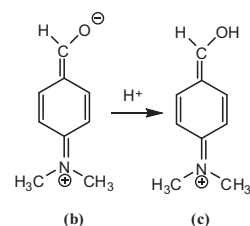
Scheme 1   Mechanism of oxidation of aldehydes by TEABC in the presence of *p*-TsOH.

This type of unusual high rate for the oxidation of *N,N*-dimethylamino benzaldehyde by benzyltrimethylammonium chlorochromate (Raju et al., 2000) and also by 4-(dimethylamino)pyridinium chlorochromate (Krishnasamy et al., 2007) have already been noticed.

3.10. Mechanism of oxidation

Under the experimental conditions employed in the present study, the substrates namely 3,4,5-trimethoxy benzaldehyde (TMBA), benzaldehyde (BA) and dimethylamino benzaldehyde (DMABA) are oxidized to the corresponding acids. Based on the above kinetic observations, i.e., the first order dependence on [Aldehyde] and [TEABC], the following mechanism is proposed for the oxidation of aldehydes by TEABC (Scheme 1). The reaction is catalyzed by hydrogen ions and the hydrogen ion dependence has the following form $k_{obs} = -a + b$ [H$^+$]. TEABC may become protonated in the presence of acid. The protonated TEABC may function as an effective

oxidant. Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. The observed solvent effect supports a transition sate, which is more polar than the reactant state. Therefore, a mechanism involving formation of chromate ester with TEABC is suggested (Scheme 1).

4. Conclusions

In this work we have studied the detailed kinetics of oxidation of TMBA, BA and DMABA in DMF–acetic acid medium by spectrophotometrically at 303 K using TEABC as an oxidant. The results of solvent effects indicate that the lowering of dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation. The order of reactivity is DMABA > BA > TMBA. In the case of oxidation of *N,N*-dimethylamino benzaldehyde the N$^+$H(CH$_3$)$_2$ group act as a

very strong electron-withdrawing group. Hence, it reacts at a very fast rate with the oxidant.

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